Isolation and Characterization of the 'Strained' Cluster Complex, $(\mu_3\text{-Bi})Co_3(CO)_6(\mu\text{-}CO)_3$; the Application of Thermogravimetric Analysis to Rational Cluster Reactions

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The thermal decomposition of $Bi\{Co(CO)_4\}_3$ in refluxing tetrahydrofuran (THF) forms the *closo* complex, $BiCo_3(CO)_9$, the structure of which has been determined by *X*-ray analysis.

The complex $Bi\{Co(CO)_4\}_3$ has been previously reported from the high yield reaction of $BiCl_3$ and $[Co(CO)_4]^-$.[1] This molecule shows an open structure similar to known BiR_3 molecules such as $BiPh_3$. Attempts to close $Bi\{Co(CO)_4\}_3$ to give $BiCo_3(CO)_9$ in analogy to the structurally characterized $BiIr_3(CO)_9$[2] were not successful, however. The obvious explanation for the reactivity difference between the cobalt and iridium systems was thought to lie in the steric bulk of bismuth, which would prevent the formation of Co–Co bonds. The larger iridium atoms could more easily form such interactions.[3] In light of our recent successes in characterizing closed geometries for Bi/Fe clusters,[4—6] it appeared plausible that a closed $BiCo_3$ species might be accessible. This hypothesis was further supported by an initial thermogravimetric study of $BiCo_3(CO)_{12}$, which showed clean loss of mass at about 100—117 °C corresponding to the loss of three carbonyls, followed by decomposition at higher temperatures (>140 °C) giving metallic bismuth and cobalt (verified by *X*-ray diffraction) with complete loss of CO (Figure 1).

Prompted by this discovery, we re-explored the thermal decomposition of $BiCo_3(CO)_{12}$ in refluxing tetrahydrofuran (THF). The reaction is complete within 30 min, and the hexane extract of this product mixture is the $(\mu_3\text{-Bi})Co_3(CO)_6(\mu\text{-}CO)_3$, formed in 56% yield. The product is soluble in hexane, toluene, diethyl ether, methylene chloride, methanol, acetone, acetonitrile, and THF. Moreover, $BiCo_3(CO)_9$ shows the following i.r. CO stretching frequencies in hexane solution: 2083m, 2041s, 2022ms, 2012m, 1981w, and 1885m cm^{-1}. The mass spectrum shows the expected parent ion peak at *m/z* 638. Elemental analyses showed excellent agreement.

This new product gives an i.r. stretching frequency that was initially surprising in that, unlike $BiIr_3(CO)_9$, it contains a bridging carbonyl resonance (ν_{CO} 1885 cm^{-1}). *X*-Ray analysis† showed the molecule unquestionably to be $(\mu_3\text{-Bi})Co_3(CO)_6(\mu\text{-}CO)_3$, in spite of crystallographic problems which include high absorption and high symmetry for data from a weakly diffracting, brown, needle-shaped crystal.

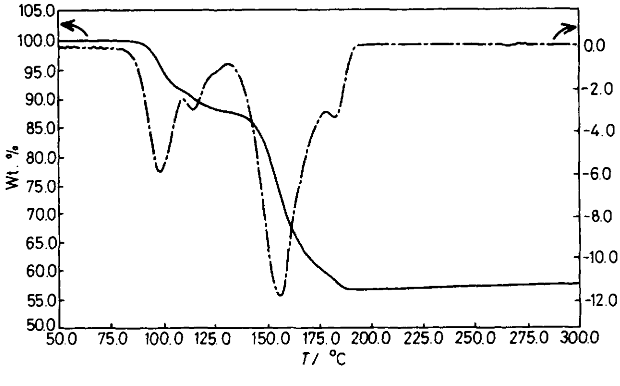

Figure 1. Thermogravimetric analysis (solid line) and first derivative (dashed line) of $BiCo_3(CO)_{12}$, measured at a heating rate of 10 °C min^{-1} in N_2. The major peak at 100 °C corresponds to a weight loss of one CO per cobalt atom. By 200 °C, weight loss indicates that all carbonyls have been removed. *X*-Ray powder data of the residue show the presence of Bi and Co metals.

The molecule sits on a three fold axis and is trisected by three mirror planes. The bismuth atom sits atop a closed Co_3 triangle with two terminal carbonyls attached to each cobalt. One bridging carbonyl lies between each Co–Co bond (Figure 2). The Co–Co distance is 2.52(1) Å, and the Bi–Co distance is 2.613(6) Å. For comparison, the Co–Co distance in $Co_2(CO)_8$ is 2.524 Å,[7] and the Bi–Co distance in $Bi\{Co(CO)_4\}_3$ is 2.766 Å.[1]

The Co–Co bond formation resulting from the thermal decomposition of $BiCo_3(CO)_{12}$ in refluxing THF is reversible, but the reaction is not fast. In hexane at 750 p.s.i. of CO, $BiCo_3(CO)_9$ is converted into $BiCo_3(CO)_{12}$ in about 6 days. These observations support the idea that $BiCo_3(CO)_9$ does not possess ring strain, in contrast to earlier predictions.

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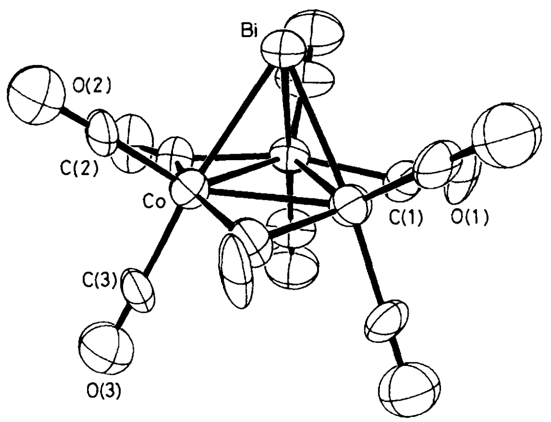

Figure 2. ORTEP diagram of $(\mu_3\text{-Bi})Co_3(CO)_6(\mu\text{-}CO)_3$ showing 50% thermal probability ellipsoids and atom labelling. Important bond distances and angles are: Bi–Co, 2.613(6); Co–Co, 2.52(1) Å; ∠ Bi–Co–Co, 61.1(1); Co–Bi–Co, 57.7(2); Bi–Co–C(1), 89(1); Co–Co–C(1), 111(1); Co–C(1)–O(1), 140(2)°.

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† *Crystal data:* $BiCo_3(CO)_9$, hexagonal, space group $P6_3mc$, $a = b = 11.076(8)$, $c = 7.301(2)$ Å, $Z = 2$, $U = 775.7(8)$ Å^3. The hexagonal, acentric condition is supported by statistical analysis of the appropriate equivalent reflections. The two possible enantiomorphs were examined, and the one chosen gave a weighted *R* value 0.8% less than the other form. Refinement converged with $R = 5.6\%$ and $R_w = 6.6\%$ for $I > 3\sigma(I)$. Atomic co-ordinates, bond lengths and angles and thermal parameters have been deposited at the University of Bonn. See Notice to Authors, Issue No. 1.

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